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The stoichiometric dependence of the modulation wave vector in the incommensurately modulated structures of ϵ -Li_xV₂O₅ and ϵ' -Li_xV₂O₅

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Abstract. Electron diffraction was used to study the stoichiometric dependence of the modulation wave vector in the incommensurately modulated structures of ϵ - and ϵ' -Li_xV₂O₅. For ϵ -Li_xV₂O₅ ($0.32 \leq x \leq 0.52$) and ϵ' -Li_xV₂O₅ ($0.52 \leq x \leq 0.80$) the space group of the basic structure is *Pmnm*, and the superspace group characterizing the one-dimensionally modulated structure is found to be *Pmnm* ($0\ \gamma\ 1/2$). The stoichiometry dependence of the modulation wave vector \mathbf{q} can be described by a staircase function, with γ being constant at $\gamma = 0.435(5)$ for ϵ -Li_xV₂O₅. A second plateau has been observed in the stability field of ϵ' -Li_xV₂O₅ for $0.550 \leq x \leq 0.575$ with $\gamma = 0.465(5)$. For the stoichiometry range $0.575 \leq x \leq 0.707$, γ varies continuously between $\gamma = 0.465(5)$ and $\gamma = 0.565(5)$.

In the present paper we will show that the system Li_xV₂O₅ can be described by an extended Frenkel–Kontorova model. Despite its extreme simplicity in the one-dimensional case, the model exhibits most of the features necessary for understanding the variation of the dependence of the modulation wave vector on the lithium stoichiometry.

1. Introduction

The phases Li_xV₂O₅ belong to a group of intercalation compounds which are formed during the topotactic intercalation reaction in which lithium ions intercalate into V₂O₅; this takes place, for example, when V₂O₅ is used as the cathode material in a reversible ambient temperature Li battery. For the stoichiometry range $0.00 \leq x \leq 1.00$, it is known that four metastable phases are formed, characterized by V₂O₅-related crystal structures. Specifically, the four phases are: α -Li_xV₂O₅ ($0.00 < x \leq 0.13$), ϵ -Li_xV₂O₅ ($0.32 \leq x \leq 0.52$), ϵ' -Li_xV₂O₅ ($0.52 \leq x \leq 0.80$), and δ -Li_xV₂O₅ ($0.88 \leq x \leq 1.00$) [1–6]. The quasi-two-dimensional layered structures are built up of edge- and corner-sharing VO₅ pyramids, forming infinite layers stacked along *c*. The intercalated lithium ions are located in the van der Waals gap between the layers. In the phases α -, ϵ -, and ϵ' -Li_xV₂O₅, the layers are stacked directly on top of each other, leading to the formation of big cubeoctahedral cavities. These cubeoctahedral cavities, composed of eight oxygen atoms of one V₂O₅ layer and four oxygens of the neighbouring one, are connected by shared fourfold faces, thus forming infinite channels along the crystallographic *b*- and *c*-axes. Along the *a*-axis, these channels are displaced by the vector $\frac{1}{2}\mathbf{b}$ and locked by VO₅ pyramids, thus hampering the

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diffusion of intercalated ions in this direction. In the δ -phase, the V_2O_5 layers are displaced by $\frac{1}{2}\mathbf{b}$, leading to tetrahedral cavities instead of cubeoctahedral sites for the intercalated Li^+ ions [7].

Recent investigations of the structure of ϵ' - $Li_xV_2O_5$ have revealed that the orthorhombic structure is incommensurately modulated at room temperature [8]. The space group of the average structure is $Pm\bar{m}n$; the $(3+1)$ -dimensional superspace group [9] was found to be $Pm\bar{m}n(0\gamma 1/2)$. The one-dimensional modulation wave vector is $\mathbf{q} = \gamma\mathbf{b}^* + \frac{1}{2}\mathbf{c}^*$.

The two phases ϵ - and ϵ' - $Li_xV_2O_5$ can be distinguished only in their low-temperature behaviour. Phases ϵ - $Li_xV_2O_5$ with $0.32 \leq x \leq 0.52$ are stable against a shear deformation, in contrast to phases ϵ' - $Li_xV_2O_5$ with $0.52 \leq x \leq 0.80$, which undergo a continuous ferroelastic phase transition on cooling [1, 3]. In this context we have studied the structure of ϵ - $Li_xV_2O_5$ by means of electron diffraction, and we will show that this phase is also incommensurately modulated at room temperature.

In the present paper, we describe the stoichiometric dependence of the modulation wave vector for the stoichiometry range $0.32 \leq x \leq 0.71$. It will be shown that the dependence is different for the two phases ϵ - and ϵ' - $Li_xV_2O_5$. The results will be discussed in terms of a Frenkel–Kontorova model [10] in its extended form derived by Frank and van der Merwe [11].

2. Experimental details

Polycrystalline ϵ - and ϵ' - $Li_xV_2O_5$ were prepared by chemical reduction of polycrystalline vanadium pentoxide by lithium iodide in acetonitrile at room temperature [2]. The lithium stoichiometry was determined by iodometric titration with a standardized aqueous $Na_2S_2O_3$ solution. The uncertainty in the lithium stoichiometry found by analysis is estimated to be of the order of 0.5%, in accordance with earlier experiments [1–5]. The purity of the samples analysed was investigated by means of x-ray powder diffraction. The determination of the lattice parameters was performed by least-squares refinements with respect to the centres of the shape-fitted Bragg peaks [12].

Electron diffraction patterns were obtained with a Philips EM400T electron microscope, using an acceleration voltage of 100 kV ($\lambda = 0.037 \text{ \AA}$) at room temperature. The samples were prepared by dispersal of the crystallites in ethanol, and subsequent deposition on a carbon support grid containing holes. The grain size of the plate-like crystals was estimated visually to be of the order of 0.5–5 μm . The thickness of the crystallites was of the order of a few hundred \AA .

The diffraction patterns were evaluated by measuring the ratios of distances between appropriately chosen reciprocal-lattice points in the photographs. The quoted standard deviation of γ is that obtained by repeated measurements of the distances between pairs of reflections. The homogeneity of the samples was investigated by determining the modulation wave vector for a large number of crystals. The observed modulation wave vector was always within the estimated standard deviation. This observation makes us sure that the samples investigated are homogeneous.

3. Results

Previous electron diffraction studies have shown that the room-temperature phase of ϵ' - $Li_xV_2O_5$ is incommensurately modulated [8]. The basic lattice crystallizes in the orthorhombic space group $Pm\bar{m}n$, with lattice parameters $a = 11.4086(2) \text{ \AA}$, $b =$

3.5640(1) Å and $c = 4.5042(1)$ Å, for a chemical composition with $x = 0.605(3)$. The satellite reflections up to third order can be indexed in the (3 + 1)-dimensional superspace group $Pm\bar{m}n$ ($0\ \gamma\ 1/2$). The modulation wave vector \mathbf{q} is one dimensional, and can be written as

$$\mathbf{q} = \gamma\mathbf{b}^* + \frac{1}{2}\mathbf{c}^* \quad (1)$$

where \mathbf{b}^* and \mathbf{c}^* are the reciprocal-lattice vectors of the basic structure. The incommensurate component γ depends on the stoichiometry.

In the present study, we have investigated different phases $\text{Li}_x\text{V}_2\text{O}_5$ with $0.32 \leq x \leq 0.71$, thus covering the ϵ - and ϵ' -phases. In the course of these investigations, we have found that both phases are incommensurately modulated at room temperature.

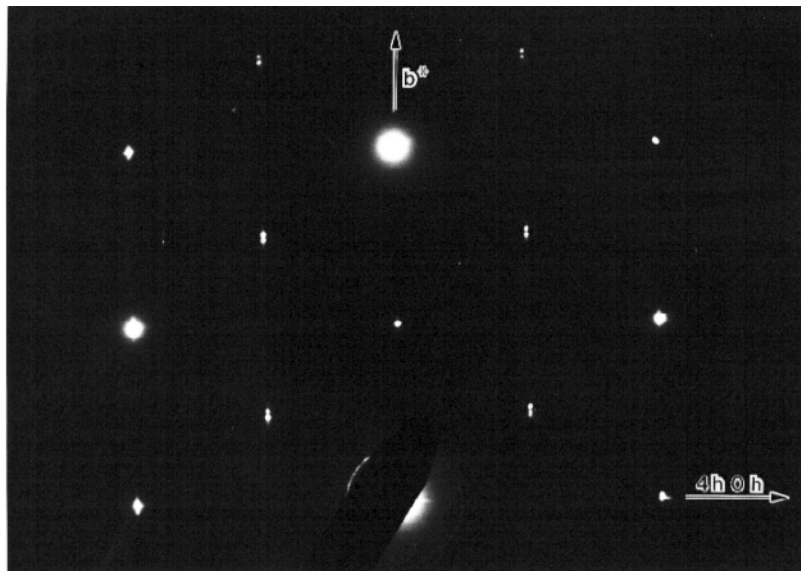


Figure 1. An electron diffraction pattern of ϵ - $\text{Li}_{0.591(3)}\text{V}_2\text{O}_5$ at 298 K (zone $[\bar{1}04]$)

Figure 1 shows an electron diffraction pattern of the zone $[\bar{1}04]$ of ϵ - $\text{Li}_{0.591(3)}\text{V}_2\text{O}_5$, taken at 298 K.

The set of observed reflections can be subdivided into two subsets. One subset consists of strong diffraction spots defining an orthorhombic lattice with space group symmetry $Pm\bar{m}n$. The second subset consists of first-, second-, and third-order satellites, which are, in general, much weaker than the main reflections. They are found at positions $\pm m\mathbf{q}$ with respect to the main reflections, where m is a small integer. All of the reflections can be indexed by four integers $hklm$, according to

$$\mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}. \quad (2)$$

The n th-order satellites have $m = \pm n$; $m = 0$ corresponds to the main reflections.

In the electron diffraction pattern, an incommensurate structure with a modulation wave vector \mathbf{q} cannot be distinguished from one with a modulation wave vector $1 - \mathbf{q}$ (see figures 2(a) and 2(c)). Nevertheless we have chosen a modulation wave vector \mathbf{q} with $\gamma < 0.5$ for phases with $x \leq 0.575$, and a modulation wave vector \mathbf{q} with $\gamma > 0.5$ for phases with $x > 0.575$ (see figures 2(a)–2(c)). If we were to always use a modulation wave vector \mathbf{q} with $\gamma < 0.5$, the corresponding \mathbf{q} -dependence would be in conflict with current theories

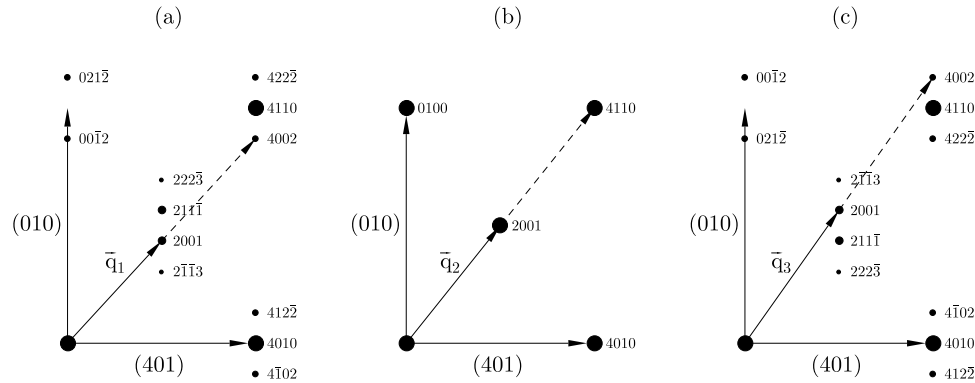


Figure 2. Schematic drawings of the dependence of the electron diffraction pattern of zone $[\bar{1}04]$ on the increasing modulation wave vector \mathbf{q} , representing phases $\text{Li}_x\text{V}_2\text{O}_5$ with increasing lithium contents: (a) $\mathbf{q}_1 = 0.435\mathbf{b}^* + \frac{1}{2}\mathbf{c}^*$, (b) $\mathbf{q}_2 = \frac{1}{2}\mathbf{b}^* + \frac{1}{2}\mathbf{c}^*$, (c) $\mathbf{q}_3 = 0.565\mathbf{b}^* + \frac{1}{2}\mathbf{c}^*$. The main reflections are indicated by large circles, and a number of first-order, second-order, and third-order satellite reflections by increasingly smaller circles. The reflections are indexed by four integers $hklm$ (see the text).

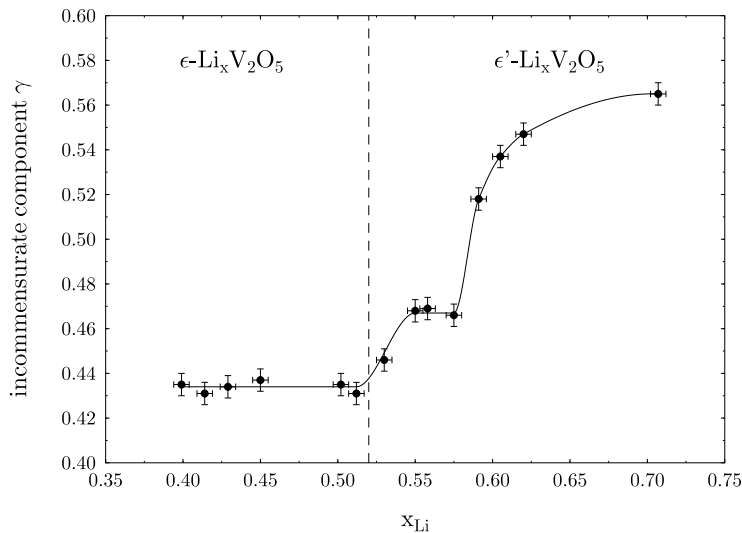


Figure 3. The incommensurate component γ of the modulation wave vector as a function of the lithium stoichiometry.

on modulated structures (see, for example, [20]). The resulting stoichiometric dependence $q_\gamma(x)$ is shown in figure 3.

The functions $q_\gamma(x)$ are different for the two phases investigated, ϵ - and ϵ' - $\text{Li}_x\text{V}_2\text{O}_5$. While γ is constant for ϵ - $\text{Li}_x\text{V}_2\text{O}_5$, it varies with the lithium stoichiometry x in the stability field of ϵ' - $\text{Li}_x\text{V}_2\text{O}_5$. The lithium concentration for the change in the behaviour of \mathbf{q} corresponds to the critical concentration for the isomorphous phase transition $\epsilon \rightarrow \epsilon'$, determined from low-temperature powder diffraction experiments [3], thus lending additional support to the notion of the existence of two isomorphous, but distinct, phases.

For the phase ϵ - $\text{Li}_x\text{V}_2\text{O}_5$, the value of γ is constant, with $\gamma = 0.435(5)$ over the whole stoichiometry range $0.32 \leq x \leq 0.52$. The constant value of γ can be considered as being part of a devil's staircase function. A second plateau is observed for $0.550 \leq x \leq 0.575$ with $\gamma = 0.465(5)$. From $x = 0.575$ to $x = 0.707$, γ increases quasi-continuously from $\gamma = 0.465(5)$ to $\gamma = 0.565(5)$. Within the resolution of our experiment, we have not observed the locking-in of q to any value of γ in this stoichiometry range. Nevertheless we cannot exclude the possibility of additional plateaus. Much higher resolution would be needed to decide on this question.

A schematic drawing of the electron diffraction patterns of zone $[\bar{1}04]$, representing phases with $\gamma < 0.5$, $\gamma = 0.5$, and $\gamma > 0.5$, is given in figure 2. For lithium concentrations x far away from a concentration $x = 0.585$, the distance between corresponding satellite reflections with $m = \pm n$ is large, whereas for chemical compositions near $x = 0.585$, the splitting is very small. In the ideal case, the two reflections should coincide in one commensurate superstructure reflection with $\gamma = 0.5$ (figure 2(b)), corresponding to a commensurate superstructure with $a' = a$, $b' = 2b$, and $c' = 2c$. Experimentally, such a commensurate twofold superstructure was not observed, possibly due to insufficient resolution.

4. Discussion

The structures of ϵ - and ϵ' - $\text{Li}_x\text{V}_2\text{O}_5$ are closely related to that of the parent structure V_2O_5 . They are built up of edge- and corner-sharing VO_5 pyramids, forming quasi-two-dimensional layers stacked directly on top of each other. This stacking sequence leads to the formation of cubeoctahedral cavities in the van der Waals gaps, suitable for the intercalation of lithium ions. These cubeoctahedral cavities share common fourfold faces, and form infinite channels along the crystallographic b - and c -axes. The distribution of the intercalated lithium ions over the available cubeoctahedral cavities is still unknown, but it is beyond any reasonable doubt that the Li^+ ions occupy off-centre positions, and that an occupation of one cubeoctahedron with more than one Li^+ ion is impossible.

The intercalation of lithium ions into the cubeoctahedral cavities does not break the orthorhombic symmetry of the host structure V_2O_5 . However, the appearance of satellite reflections at incommensurate positions clearly demonstrates that the three-dimensional translation symmetry is broken. The deviation from the average structure is periodic, but incommensurate with the basic lattice. The satellite reflections have been observed in electron diffraction experiments only, and not with x-rays. To exclude the possibility that the satellites are just a result of an electron-beam-induced effect, we have investigated a large number of crystals for different exposure times and different beam current intensities. Neither of these variations in conditions influenced the modulation wave vector. Therefore, the fact that the incommensurate superstructure reflections have been observed only in electron diffraction experiments indicates that only weak scatterers for x-rays are affected by the modulation. Thus, significant displacements of the oxygen and vanadium atoms can be excluded, and displacements and/or ordering of the lithium ions remain as the most probable explanation. The fact that the modulation wave vector has components along b^* and c^* indicates that ordering of the lithium ions in the channels parallel to b and c must be responsible for the formation of the modulated structure.

The V_2O_5 structure with its regular array of cubeoctahedral cavities creates an 'external' periodic potential for the intercalating lithium ions. In principle, this potential would 'try' to lock the system into a commensurate configuration. However, it has to compete with strong repulsive Coulomb forces between intercalated lithium ions, which will tend to

form a regular distribution of the intercalated ions. In general, this distribution would be incommensurate with the periodic array of cubeoctahedral cavities. The strengths of the two competing interactions then determine the type of the modulation, i.e. the formation of chaotic structures, or commensurate or incommensurate superstructures.

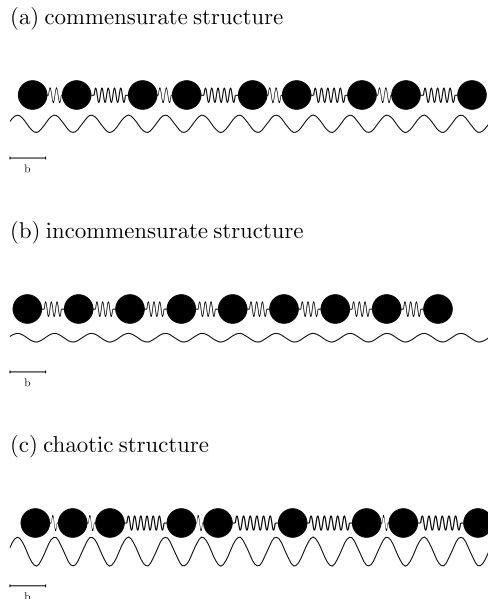


Figure 4. The one-dimensional Frank and van der Merwe model. The springs represent interactions between atoms, the wavy line the periodic potential. (a) Commensurate structure, (b) incommensurate structure, and (c) chaotic structure.

Such a system with two competing interactions can be described theoretically in terms of a Frank and van der Merwe model [11]. This model, with a sinusoidal potential, was originally introduced by Frenkel and Kontorova [10], and was subsequently studied by several authors, in particular by Frank and van der Merwe [11], Theodorou and Rice [13], Aubry [14], Green [15], and Bak [16, 17]. The one-dimensional Frank and van der Merwe model is illustrated in figure 4. It consists essentially of a chain of atoms connected by harmonic springs interacting with an underlying periodic potential of period b . Depending on the strengths of the different interactions, commensurate, incommensurate, or chaotic order may occur. In our case, the competing interactions are $\text{Li}^+ - \text{Li}^+$ repulsion and $\text{Li}^+ - [\text{V}_2\text{O}_5]^-$ attraction and repulsion.

The energy function of the system is composed of two essential terms, an elastic energy term, taking account of the repulsive forces represented by the harmonic springs between neighbouring atoms, and a term for the potential energy, given by the periodic potential of the basic lattice [17]. The microscopic energy of the Frenkel–Kontorova model is given as equation (3):

$$E = \sum_n \left[\frac{1}{2b^2} (x_{n+1} - x_n - a_0)^2 + V \left(1 - \cos \frac{2\pi}{b} x_n \right) \right]. \quad (3)$$

The total energy E of the system is given by the sum over all n atoms of the chain. The first term represents the elastic energy, where x_n is the position of the n th atom and a_0 is the lattice constant of the chain, in the absence of the periodic potential with period b ,

expressed in the second term. V is the amplitude of the periodic potential. In the absence of the periodic potential, the harmonic term would favour a lattice constant $a = a_0$ which, in general, would be incommensurate with b : the chain then forms an incommensurate structure (figure 4(b)). On the other hand, strong potential forces would force the lattice to relax into a commensurate structure with $a = nb$ (figure 4(a)). Even in cases where the potential is not strong enough to force the chain into commensurability, the potential will always modulate the chain. If the potential is very strong compared with the elastic term, it is possible to distribute the atoms randomly among the potential minima (figure 4(c)). In this case the formation of a chaotic structure is observed.

Both energy terms, the elastic energy and the potential energy, depend on external parameters, such as temperature, pressure, and chemical composition. When one of the external parameters changes, the modulation wave vector q , in general, changes too. Possible ways in which the modulation wave vector can change as some parameter is varied are known as the devil's staircase (see, for example, [17]).

The problem with such a simple model is that one would expect a continuous variation of the modulation wave vector q because of the two stoichiometry-dependent energy terms in the Frank and van der Merwe model. In addition, one would expect a commensurate twofold superstructure for $x = 0.5$, which is not found experimentally.

A comprehensive understanding of the behaviour of the modulation wave vector as a function of the lithium stoichiometry requires a third, stoichiometry-independent interaction to explain the periodicity of the system. A possibility for a third competing interaction is provided by the Friedel oscillations [19] in the V_2O_5 conduction band induced by a Li^+ ion acting as an impurity. The period l_F of these oscillations is in principle independent of the lattice constant of the V_2O_5 substructure. Assuming the Friedel oscillations to be independent of the different Li^+ ions, an effective $\text{Li}^+\text{-Li}^+$ interaction potential results, with a periodicity of l_F . Between Li^+ ions, distances are favoured, for which the maxima in the charge distribution in the V_2O_5 electron bands induced by one Li^+ ion coincide with the maxima induced by the neighbouring Li^+ .

Friedel oscillations provide an explanation for the behaviour found for low concentrations of Li^+ (the ϵ -phase). On decreasing the concentration of Li^+ , the direct Coulomb interaction of Li^+ ions becomes gradually less and less important. A possible order of Li^+ is then determined by the potential generated by Friedel oscillations and the $\text{Li}^+\text{-V}_2\text{O}_5$ potential. The periodicity of this order then will be governed by the strength and periodicities of both interactions, all of these quantities being constant for low concentrations of Li^+ . The periodicity of the Li^+ order thus should become independent of the concentration (or tend asymptotically towards a limiting value). Experimentally, we have found that $\gamma = 0.435(5)$ for $x \leq 0.52$. Alternatively, the observation of a constant value of γ can be interpreted as a lock-in at the commensurate value $7/16 = 0.4375$.

At higher concentrations of Li^+ , e.g. in the ϵ' -phase with $x > 0.52$, the direct interaction between Li^+ ions becomes more important. (Note that for $x < 0.5$ it is always possible to surround Li^+ by empty cubeoctahedral holes, whereas for $x > 0.5$, it is necessary to have neighbouring cubeoctahedral holes occupied by Li^+ ions. This most probably introduces a strong repulsive contribution to the lattice energy.) This interaction is concentration dependent, and one expects the period of the ordering to depend on the concentration, too, as found experimentally.

The concentration dependence of γ represents a devil's staircase with another plateau for $0.550 \leq x \leq 0.575$ with $\gamma = 0.465(5)$ or $7/15 = 0.467$. Within the resolution of our experiment there is no lock-in at the simple values $6/13$ and $5/11$ between the observed ones; in particular, there is no lock-in at $1/2$. With our present knowledge we cannot explain why

lock-in is only observed at 7/16 and 7/15. Insufficient resolution for the stoichiometry x may be one reason, but possibly not the only one.

The highest value for γ was found for the highest measured lithium concentration of $x = 0.707$ with $\gamma = 0.565(5)$. To a first approximation, the modulation wave vector expresses the ratio of the lattice parameters b and b' of the two sublattices V_2O_5 and Li. The increase of the lithium stoichiometry results, in general, in a decrease of the interionic distances between neighbouring lithium ions, and therefore in an increase of the incommensurate component γ . The value of $\gamma = 0.565$ seems to express a minimum value for the interionic Li^+-Li^+ distances. This can be understood as being a consequence of the increase in the harmonic energy term. For sufficiently high lithium concentrations, the repulsion becomes so strong that the system has to undergo a phase transition in order to minimize the interionic interactions. Such a phase transition can be observed for $x = 0.8$; the resulting phase is the so-called δ -phase, with a different V_2O_5 sublattice (see section 1).

The observed stoichiometry dependence is in accordance with the theory of the Frank and van der Merwe model. Depending on the strengths of the competing interactions, complicated phase diagrams with several high-order commensurate and incommensurate phases—known as the different types of staircase—can be predicted from the theory of the Frank and van der Merwe model. For the theoretical background of the devil's staircase, see, for example, Bak [17] and Aubry and Le Daeron [18].

The different behaviours of q are in accordance with the different low-temperature stabilities of the two phases. The phase boundary at $x = 0.52$ corresponds to the critical concentration for the isomorphous stoichiometry-induced phase transition $\epsilon-Li_xV_2O_5 \rightarrow \epsilon'-Li_xV_2O_5$ [3].

5. Conclusion

Electron diffraction has revealed that the orthorhombic room-temperature phases of $\epsilon-Li_xV_2O_5$ and $\epsilon'-Li_xV_2O_5$ are incommensurately modulated. The space group of the average structure is $Pm\bar{m}n$; the $(3+1)$ -dimensional superspace group is found to be $Pm\bar{m}n(0\gamma 1/2)$. The modulation wave vector is one dimensional for both phases, and is given by $q = \gamma b^* + \frac{1}{2}c^*$. The stoichiometry dependence of the wave vector is significantly different for ϵ - and ϵ' - $Li_xV_2O_5$. The incommensurate component γ is constant at $\gamma = 0.435(5)$ for $\epsilon-Li_xV_2O_5$ with $0.399 \leq x \leq 0.512$, and at $\gamma = 0.465(5)$ for $\epsilon'-Li_xV_2O_5$ with $0.550 \leq x \leq 0.575$, but is a smooth function of the lithium concentration for the stoichiometry range $0.575 \leq x \leq 0.707$.

The variation of q can be understood in terms of an extended one-dimensional Frank and van der Merwe model. The energy function of the Frenkel–Kontorova model with two competing energy terms—elastic energy due to repulsive Li–Li interaction on one hand, and potential energy due to the underlying periodic V_2O_5 potential on the other hand—must be extended to a third term, describing a periodic potential with minima separated by a period l_F , determined by the Friedel oscillations in the V_2O_5 electron bands. Because of the small number of intercalated ions and therefore weak Li^+-Li^+ interactions, the two stoichiometry-independent periodic potentials dominate in the ϵ -phase, while the elastic energy term increases in $\epsilon'-Li_xV_2O_5$ and leads to a variation in the dependence of q on x .

The formation of incommensurate modulated structures is the first and very important evidence of a Li ordering process in the intercalated V_2O_5 bronzes ϵ - and $\epsilon'-Li_xV_2O_5$. Furthermore, the new results are of great importance for the comprehension of the intercalation mechanism, and for the understanding of the various compositionally and thermally induced phase transitions.

In the present paper we have concentrated on the structural features of the modulated phases at room temperature, and the stoichiometry dependence of the modulation wave vector. Future investigations will focus on the temperature dependence, with particular consideration of the ferroelastic low-temperature phase transition in ϵ' - $\text{Li}_x\text{V}_2\text{O}_5$, and the high-temperature phase transitions $\epsilon \rightarrow \beta$ and $\epsilon \rightarrow \gamma$.

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